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Post-plasma catalytic technology for the removal of toluene from indoor air: Effect of humidity

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ABSTRACT

Hybrid plasma catalyst technology has great potential for indoor air purification. However, humidity is a critical parameter in plasma catalytic processes. In this work, several catalysts were tested downstream of a DC corona discharge and the effect of humidity was investigated on both ozone and toluene removal. Next, sorption measurements onto the catalysts were performed for toluene, trichloroethylene and acetone, using an equilibrium partitioning in closed system procedure to explain the obtained results in a quantitative manner.

Catalytic ozone decomposition experiments indicated that catalyst properties have a strong impact on the hybrid plasma catalyst performance. While the effect of humidity on catalytic ozone abatement proved to be negligible, a negative effect was observed on post-plasma catalytic (PPC) toluene removal. Indeed, for an energy density of 10 J L^{-1} using one type of Pd/Al_2O_3 as PPC, removal efficiencies were >90 and 39% at dry and 74% RH (25 °C), respectively. Nevertheless, even at 74% RH and an energy density of 10 J L^{-1}, the toluene removal efficiency was still two times higher than in the absence of a catalyst. For the first time, a logarithmic relationship has been established between VOC sorption and plasma catalytic VOC degradation results ($R^2 = 0.982$, $n = 4$). Based on the total free energy of adsorption it is suggested that the negative humidity effect on PPC is mostly due to changing Van der Waals interactions.

1. Introduction

Volatile organic compounds (VOC) in indoor environments have been suspected to cause "sick-building" symptoms like headache, eye and mucous membrane irritation, fatigue, and asthmatic symptoms [1,2]. Next to that, other parameters such as inorganic pollutants, particulate matter, biological pollutants, temperature and humidity are important for the indoor air quality. Humidity levels are optimally controlled between 30 and 60%. Air that is too dry is harmful for building structural integrity and human health. Excess humidity is a breeding ground for mold, pests, and rot in homes and is more likely to cause heart stroke, heat exhaustion, headaches, and dehydration.

Van Durme et al. [3] reported that the combination of heterogeneous catalysts with non-thermal plasma offers great potential as indoor air purification technology, particularly toward VOC degradation. Catalysts can be introduced in (in plasma catalysis (IPC)) or downstream from the discharge zone (post-plasma catalysis (PPC)). One of the most important by-products in a non-thermal plasma discharge in air is ozone. Although the decomposition of ozone into oxygen is a thermodynamically favoured process, ozone is thermally stable up to 250 °C, and a post-plasma catalyst is necessary for decomposition at lower temperatures [4]. The positive effect of PPC is the result of two different phenomena: plasma physical chemistry and heterogeneous catalysis. At the plasma stage VOC are partially oxidized, simultaneously, ozone is generated and supplied to the post-plasma zone. In the post-plasma zone, both VOC adsorption and oxidation by newly formed active species occur on the catalyst. These active species result from the catalytic ozone decomposition with formation of molecular and highly active atomic oxygen [5,6]. This phenomenon has been described for a number of catalysts such as silica gel, porous alumina, and metal oxides [4,7]. For a gas stream containing 500 ppb_v of toluene and having a RH of 26%, the highest removal efficiency was obtained with 10 g $CuOMnO_2/TiO_2$ in the downstream position. Compared with values obtained using

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Abbreviations: DC, direct current; EPICS, equilibrium partitioning in closed system; FID, flame ionisation detector; GC, gas chromatograph; HA, hydrogen acceptor; HD, hydrogen donor; IPC, in-plasma catalysis; *K*, equilibrium partitioning coefficient; LOD, limit of detection (ppb_v); ppb_v, parts per billion (=µL m^{-3}); PPC, post-plasma catalysis; ppm_v, parts per million (=mL m^{-3}); RH, relative humidity; SSA, specific surface area ($m^2\ g^{-1}$); VdW, Van der Waals interaction; VOC, volatile organic compounds.

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plasma alone, toluene, ozone and NO_2 outlet concentrations were reduced by a factor of 2.6, 2.5 and 7.0, respectively, in PPC configuration. However, for both the IPC and PPC configurations, the relative humidity of the treated gas stream showed to be a critical parameter, having a limiting effect on the plasma catalytic toluene oxidation [3]. Also Zhang et al. [8] reported a negative impact on (photo)catalytic performances when treating humid air.

In this work, the effect of humidity on both ozone and toluene removal in a hybrid post-plasma catalytic device is investigated in a more systematic and fundamental manner. Therefore, six different catalysts were tested downstream a DC corona discharge at relative humidities (RH) ranging between 0 and 72% at 25 °C; and the effect of water molecules on the synergetic power observed during PPC is investigated in more detail. In order to better understand the observed results, equilibrium sorption constants of toluene on the selected catalysts were determined as a function of the RH using the EPICS methodology [9].

This quantitative approach provides new insights on the effect of humidity on PPC systems, and for the first time, a relationship has been established between sorption data and plasma catalytic VOC degradation results.

2. Experimental

2.1. Post-plasma catalytic reactor

A positive four pins-to-mesh corona reactor is mounted in a cylindrical tube with an inner diameter of 42 mm. A set of four crenellated inox pins are placed towards a stainless steel cathode mesh. Each pin is ballasted with a 1.5 MΩ resistor and the total current is equally distributed over each pin. The inter-electrode gap was set at 20 mm, and the discharge is powered by a 40 kV/5 mA DC high voltage supply. During this work, two 4-pins-to-mesh modules are placed in series. The catalysts are introduced downstream to these plasma reactors. Details of the plasma reactor can be found in Van Durme et al. [10]. For removal experiments, a gas stream with a gas flow rate of typically 10 L min^{-1} was loaded with toluene using a capillary diffusion system [10]. During these experiments, energy densities of the plasma ranged between 0 and 50 J L^{-1}.

2.2. Heterogeneous catalysts

Six different catalysts, divided in two subgroups, were selected in this study, each having unique physical–chemical properties.

In the first set, containing four catalysts (supplied by Hereaus (Hanau, Germany)), the active compound is deposited on a support material. Two catalysts contain Pd (0.5 wt%) as the active compound with different types of Al_2O_3 as a support material (Pd/Al_2O_3(a) and Pd/Al_2O_3(b)). The active material in two other catalysts involves a mixture of CuO (3 wt%) and MnO_2 (6.8 wt%) deposited on a TiO_2 support (Cu–Mn/TiO_2(a) and Cu–Mn/TiO_2(b)). According to the supplier, the BET specific surface area and the pellet size of Pd/Al_2O_3(a), Pd/Al_2O_3(b), Cu–Mn/TiO_2(a) and Cu–Mn/TiO_2(b) catalysts amounts 230, 280, 32 and 50 $m^2\,g^{-1}$, and 2–4, 2–5, 1.5 and 1.5 mm, respectively.

In the second set of catalysts the active compound is dispensed in the bulk of the material. Two such catalysts, N150 and N140, were supplied by Süd-Chemie (München, Germany). The first contains >40 wt% Fe_2O_3 and >25 wt% MnO_2 as active compounds, with an average particulate size of 6 mm and a specific BET surface area of 100 $m^2\,g^{-1}$. The latter contains >15 wt% CuO and >25 wt% MnO_2, with an average pellet size of 5 mm and a specific BET surface area of 100 $m^2\,g^{-1}$.

Hybrid plasma catalytic experiments were only started when equilibrium was reached between the heterogeneous catalyst and the initial toluene concentration. Therefore, inlet and outlet concentrations were compared using GC–FID until they were equal for at least 60 min.

2.3. EPICS methodology

Equilibrium adsorption constants K (mL g^{-1}) were determined using an optimized equilibrium partitioning in closed systems (EPICS) methodology [9,11–14]. Three clean and dry vials were filled with an appropriate amount of catalyst ($m = 0.4 \pm 0.1$ g) and closed gas tight using Mininert valves (Alltech Ass., Lokeren, Belgium). Next, each vial was flushed for at least 8 h with clean air (Air Liquide, Luik, Belgium) having a controlled relative humidity. Air humidity was set by bubbling dry air (<1% RH) through a cooled water column. In a next step, a known amount of toluene, trichloroethylene and acetone, was introduced in all two-phase systems. Three VOC were injected to quantitatively determine catalyst properties (detailed discussion in Section 3.3). In a similar way, three one-phase vials containing no catalyst material, were loaded with an identical mass of VOC (resulting concentration$_{VOC}$ = 125 ppm_v). To avoid photolytic effects, both one- and two-phase systems were wrapped into aluminium foil during incubation at 25.0 ± 0.1 °C for at least 8 h. Headspace sampling was done using a 0.5 mL gas syringe (Alltech Ass.) followed by GC injection.

The equilibrium adsorption coefficient K (mL g^{-1}) is calculated according to Eqs. (1) and (2) [9]:

$$K = \frac{rV_{g,1} - V_{g,2}}{M_{catalyst}}\,(\mathrm{mL\,g^{-1}}) \qquad (1)$$

where

$$r = \frac{C_{g,1}/m_1}{C_{g,2}/m_2} \qquad (2)$$

With m_1 and m_2 (g) the mass of VOC in one and two-phase system; $M_{catalyst}$ the mass of catalyst material (g); and $V_{g,1}$ (mL), $V_{g,2}$ (mL) and $C_{g,1}$ (g mL^{-1}) and $C_{g,2}$ (g mL^{-1}) the gas volumes and equilibrated VOC concentration of the one- and two-phase systems, respectively.

2.4. Analytical methods

At inlet and outlet sampling ports, gas sampling was done using solid-phase microextraction (SPME) with a 100 μm polydimethylsiloxane fibre (Supelco) with an extraction time of 15 min [10]. Temperature effects on the SPME efficiency were investigated, but proved not to be significant in this study. A SPME liner was installed in a Agilent 6890 Series gas chromatograph having a split-splitless injector set at 220 °C. After separation on a cross linked methyl siloxane capillary column (length of 30 m, column diameter of 0.53 mm, film thickness 5.0 μm (HP-1) (HP, Santa Clara), the analytes were detected using a flame ionisation detector (FID) and peak areas were integrated with HPCORE integration software. The FID detector (250 °C) was fed by 400 mL min^{-1} air and 40 mL min^{-1} hydrogen. The carrier gas was helium with a flow rate of 3 mL min^{-1}. Analyses were carried out isothermally (140 °C). Equilibrated water–gas systems with a known toluene headspace concentration were used for calibration [14]. A limit of quantification, corresponding to a signal-to-noise ratio of 10, was determined to be 67 ppb_v.

Ozone was monitored using an Anseros ozone analyzer (UV at 253 nm) equipped with Picolog Acquisition software. Therefore, a constant gas flow of 200 mL min^{-1} was pumped from a sample point to the detector. Temperature and humidity monitoring was conducted with a TESTO 110 device. For current and voltage

measurements, two multimeters (Velleman DVM 92) were used in order to measure the real energy input into the plasma.

3. Results and discussion

3.1. Post-plasma catalysis: ozone decomposition

3.1.1. Effect of catalyst characteristics on ozone decomposition

Fig. 1 represents the concentration of ozone which is produced by the DC corona discharge ('no catalyst'-curve) next to ozone outlet concentrations after passing the heterogeneous catalysts.

Results indicate that both physical and chemical properties of the catalyst materials strongly affect ozone decomposition efficiencies obtained in PPC configuration. Indeed, when 15 g of Pd/Al_2O_3(a) is introduced in the reactor, ozone outlet concentrations are reduced by 94%, while this is only 48% using an equal mass of N150 catalyst. This might be explained by a difference in BET specific surface area, being 230 and 100 $m^2\,g^{-1}$ for Pd/Al_2O_3(a) and N150, respectively. On the other side, a similar ozone removal is obtained for both Pd/Al_2O_3 catalysts despite a difference in specific surface area (SSA) (230 $m^2\,g^{-1}$ vs. 280 $m^2\,g^{-1}$). Among the catalysts investigated, these Pd/Al_2O_3 catalysts are the most efficient towards ozone decomposition. This indicates that SSA is not always the main parameter affecting catalytic ozone decomposition. This is supported by comparing experimental data obtained for Cu–Mn/TiO_2(a) with those of N140 showing similar ozone degradation data, but having different SSA of, respectively, 32 and 100 $m^2\,g^{-1}$ (Fig. 1). N150, having a SSA of 100 $m^2\,g^{-1}$, is less efficient in ozone decomposition than Cu–Mn/TiO_2(a), having a SSA up to a factor 3 lower.

Our measurements reveal that mainly the active compound, rather than the presence of a support material and the SSA of the catalyst, determines the rate of ozone decomposition. Differences in ozone decomposition when using other active compounds can be explained by the existence of different decomposition mechanisms. Radhakrishan et al. [15] suggested that ozone decomposition on a MnO_x/Al_2O_3 catalyst occurs through an electron transfer from Mn^{n+} to an ozone molecule. In this way, ozone is decomposed into an oxygen molecule and an atomic oxygen. Next, unstable O_2^{2-}–$Mn^{(n+2)+}$ complexes decompose by reducing the oxidized manganese back to Mn^{2+} and desorption of an oxygen molecule. Similar mechanisms can be observed for other metal oxides (e.g. FeO catalysts) or noble metals (e.g. Pd) [16]. On the other hand, Rakitskaya et al. [17] reported other processes for

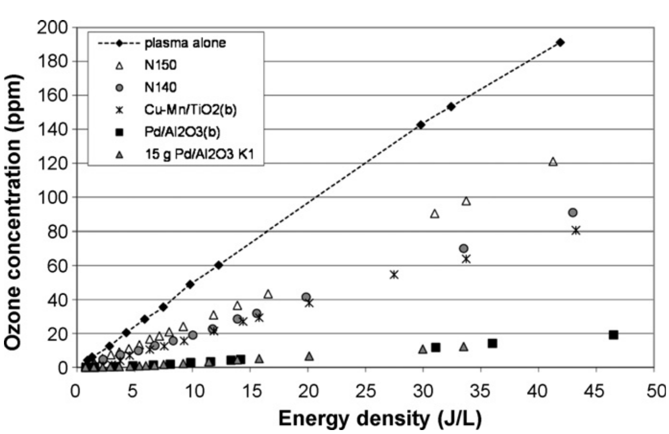

Fig. 1. Ozone production (plasma alone) and ozone outlet concentrations (ppm_v) after passing the catalyst bed as a function of energy density ($J\,L^{-1}$) applied to positive DC corona discharge and the type of heterogeneous catalyst ($m_{catalyst}$ = 15.0 g, Q = 10.0 L min^{-1}, P = 101.3 kPa, T = 25.0 °C, dry air) (AC: active compound, S: support).

Co(II)-catalyst used for ozone degradation. For these catalysts the role of water molecules is important. There is a fast formation of HO_2 due to the reaction of ozone and a hydroxyl radical (produced from catalytic reaction between water and atomic oxygen). It can be concluded that the catalytic activity of supported metal complexes is essentially influenced by the specific interactions with certain surface groups (active compound type), and consequently by the nature of support material [17].

3.1.2. Effect of humidity on ozone decomposition using catalysts in PPC position

Humidity strongly affects ozone production rates in plasma. Indeed, for an energy density of 10 $J\,L^{-1}$ in dry air, the ozone concentration in the plasma outlet gas stream is 48.9 ppm_v. The ozone production in the plasma decreases at higher humidities; an outlet ozone concentration of 28.4 ppm_v is monitored at 35% RH, and 18.9 ppm_v at 74% RH.

The effect of humidity on catalytic ozone decomposition is examined by passing dry and humidified air (0% < RH < 74%) through the reactor containing 15 g of the most promising catalyst material (Pd/Al_2O_3(b)) (Fig. 2). When using Pd/Al_2O_3(b)-based post-plasma catalysis, the ozone outlet concentrations decreased to 2.9 ppm_v in dry air; and to 3.8, 3.7 and 2.0 ppm_v as RH = 26, 35 and 74%, respectively. In conclusion, for all tested humidity levels the relative ozone decomposition efficiency amounted 89 ± 3%. Similar results were obtained for other energy densities (0% < RH ≤ 74%). Based on this data, a linear relationship could be observed between ozone production levels (ppm_v) and the amount of ozone removed (ppm_v) in the PPC unit containing 15 g Pd/Al_2O_3(b) (Fig. 2). This proves that humidity (0% < RH ≤ 74%) has no direct effect on the catalytic activity of Pd/Al_2O_3 towards ozone decomposition.

In agreement with these findings, Sekiguchi et al. [18] and Sullivan and Thornberry [19] reported an RH independent catalytic ozone degradation in similar RH range on MnO_2 and alumina, respectively. This might be surprising given the large amounts of water that adsorb on these catalyst materials. Raoof et al. [20] reported that typically a few layers of water (<10) are adsorbed on silica surfaces in humid air (<90% RH). During catalytic ozone conversion processes in these conditions, hydroxyl radicals might be produced influencing the net ozone degradation performance [3]. Secondly, water might also compete with ozone for catalyst

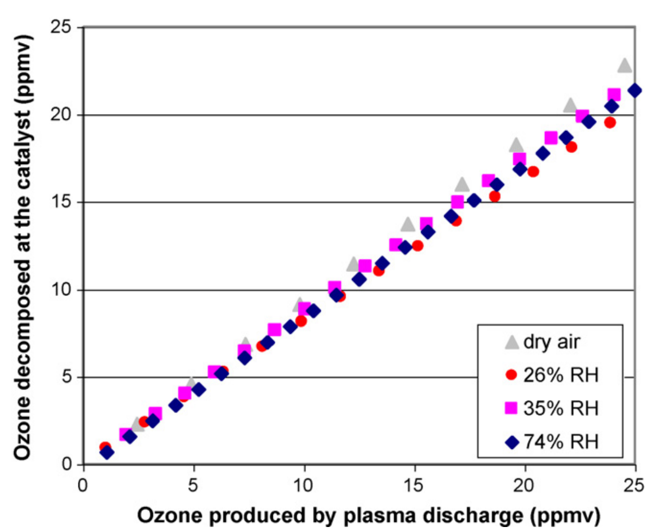

Fig. 2. Relation between inlet ozone concentration (ppm_v) and amount of ozone removed in PPC unit using Pd/Al_2O_3(b). Experiments were done in dry air and at RH = 26, 35 and 74% ($m_{catalyst}$ = 15.0 g, Q = 10.0 L min^{-1}, P = 101.3 kPa, T = 25 °C).

sorption sites [3]. The fact that no negative effect of humidity is observed on the catalytic ozone degradation during this study, can be explained by three possible phenomena. First, the reactive ozone chemistry might be considerably more exothermic than the water/catalyst physisorption, secondly the ozone diffusion through multilayers of sorbed water could be fast enough to prevent mass transfer limitation, and finally it is possible that water simply adsorbs at sites which are physically separated from the sites reactive for ozone [19].

3.2. Post-plasma catalysis: toluene degradation

3.2.1. Effect of catalyst characteristics on toluene degradation

Since the amount of converted ozone is directly correlated with the concentration of newly formed oxidative species at the catalyst surface (e.g. atomic oxygen), similar trends for PPC toluene oxidation are expected like those observed during ozone decomposition experiments (Fig. 1). Tidahy et al. [16] confirms that the catalyst support plays an important role in catalytic VOC oxidation. Therefore, toluene degradation experiments were performed in dry air using different catalysts in the downflow position (PPC). The selected catalysts, i.e. Pd/Al_2O_3(a), Pd/Al_2O_3(b), Cu–Mn/TiO_2(a), Cu–Mn/TiO_2(b), N140, N150, were in equilibrium with initial toluene concentrations. For all cases, resulting toluene outlet concentrations in dry air using a plasma energy density of only 2.5 J L^{-1}, decreased below the limit of detection (67 ppb_v) representing a PPC toluene removal efficiency of at least 90%. Contrary, in the absence of catalysts material less than 10% toluene removal efficiency was measured. Next, hybrid catalyst plasma technology resulted in a strong decrease of oxidation by-products (<LOD) compared when using isolated plasma [10]. This might indicate that hybrid plasma catalyst technology increases the total mineralization rate. However, CO and CO_2 measurements have to be done in future research to confirm this.

Due to the very high removal efficiencies, no conclusions can be made with respect to the effect of catalyst type on toluene removal in dry air. However, it is proven that in dry conditions the heterogeneous reaction pathway is much more important than the homogeneous degradation pathway in plasma catalytic processes. Tidahy et al. [16] reported that the catalyst support plays an important role in catalytic VOC oxidation at dry conditions.

3.2.2. Effect of humidity on PPC toluene degradation

The post-plasma catalytic toluene removal in humid air has been investigated in two series of experiments. First, toluene removal has been determined in a PPC unit, treating a 10 L min^{-1} gas stream enriched with 0.5 ppm_v of toluene and a RH of 30, 51 and 72%. At an energy density of 10 J L^{-1}, toluene removal efficiencies amounted to 61, 50 and 39%, respectively. This indicates the adverse effect of humidity on Pd/Al_2O_3(b) PPC toluene removal, being in agreement with recent results obtained with a Cu–Mn/TiO_2 catalyst [3]. PPC toluene decomposition in dry air is shown to be up to 5 times more efficient than in air streams of 50% RH. However, even for the highest relative humidity (72%), toluene degradation is still 2 times higher than in the absence of a catalyst. This proves the importance of PPC even in humid conditions.

Secondly, the catalytic activity of four different catalysts towards toluene degradation has been compared with each other at a relative humidity of 50% and at energy densities between 2 and 20 J L^{-1} (Fig. 3).

It is proven that for identical relative humidity (RH = 50% at T = 25 °C), significant differences in PPC toluene removal efficiency exist between the selected catalysts. For example, the toluene removal efficiency obtained in air with 50% RH and an energy

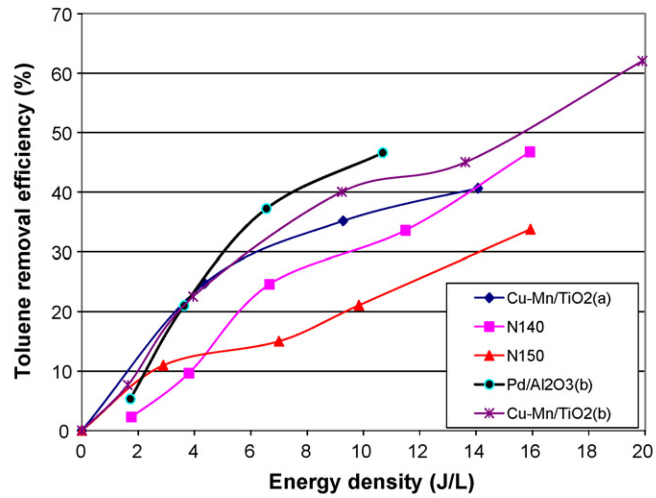

Fig. 3. Toluene degradation efficiencies in humid air (50% RH) for different catalysts (Cu–Mn/TiO_2(a), N140, Pd/Al_2O_3(b), N150) positioned in post-plasma position ($m_{catalyst}$ = 15.0 g, Q = 10.0 L min^{-1}, inlet concentration toluene = 0.5 ppm_v, T = 25 °C, P = 101.3 kPa).

density of 4 J L^{-1} using Cu–Mn/TiO_2(a) and N140 as PPC catalysts, amounts to 25 and 10%, respectively. However, Fig. 1 shows that for both catalysts, a similar amount of ozone is decomposed in the catalytic bed. This indicates that next to ozone decomposition, also other processes play an important role towards toluene decomposition. From Fig. 3 it is also seen that homogeneous reactions [10] becomes equally important compared to heterogeneous reactions under humid conditions.

Third, PPC experiments performed with 15 g Pd/Al_2O_3(b) at 8% ≤ RH ≤ 72% revealed that toluene removal correlates well with ozone decomposition at the catalyst surface (Fig. 4). This can be explained by the increased production of new oxygen active species from O_3 on the catalyst surface.

Fig. 4 also shows that for an equal amount of converted ozone, toluene is removed more efficiently at lower relative humidities. Indeed, when 10.2 ppm_v of ozone is catalytically decomposed, 0.3 ppm_v of toluene (C_{in} = 0.5 ppm_v) is removed at 8% RH, while this is only 0.2 ppm_v at RH between 30 and 72%. Thus, results presented in both Figs. 3 and 4 show that not only the amount of newly formed active species determines the catalytic toluene removal efficiency.

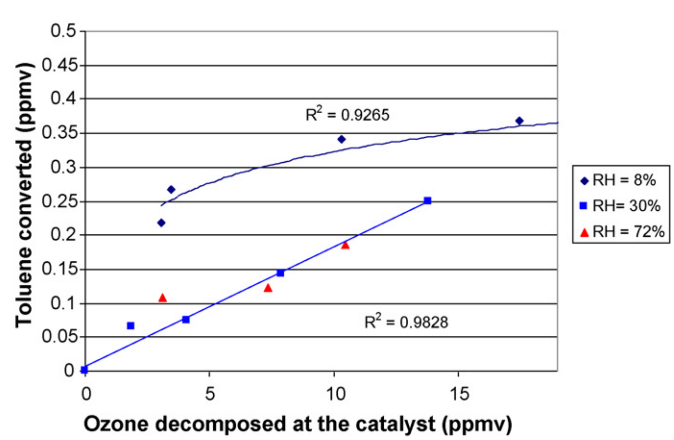

Fig. 4. Converted toluene (ppm_v) as a function of removed ozone (ppm_v) for Pd/Al_2O_3(b) PPC configuration at three relative humidities (8, 30, 72% RH) ($m_{catalyst}$ = 15.0 g, Q = 10.0 L min^{-1}, inlet concentration toluene = 0.5 ppm_v, T = 25 °C, P = 101.3 kPa).

Table 1
Effect of relative humidity on the sorption coefficient K (mL g^{-1}) of three relevant indoor air pollutants (toluene, TCE, acetone) and VdW and electron donor/acceptor properties (mJ $m^{-2})^{0.5}$ of three PPC catalysts (Pd/Al_2O_3(b), Cu–Mn/TiO_2(b), N150) (P = 101.3 kPa, T = 25 °C)

Catalyst	RH (%)	$K_{toluene}$ (mL g^{-1})	K_{TCE} (mL g^{-1})	$K_{acetone}$ (mL g^{-1})	VdW* (mJ $m^{-2})^{0.5}$	EA* (mJ $m^{-2})^{0.5}$	ED* (mJ $m^{-2})^{0.5}$
Pd/Al_2O_3(b)	<1	62,500 ± 600	12,100 ± 900	103,300 ± 22,700	10.2	4.0	4.2
	8	5,020 ± 520	430 ± 20	19,500 ± 1,100	7.4	4.8	3.0
	17	1,490 ± 180	350 ± 40	1,320 ± 910	6.2	4.7	2.9
	31	790 ± 50	200 ± 20	5,190 ± 420	5.6	4.3	2.6
	37	650 ± 50	180 ± 20	4,300 ± 530	5.4	4.2	2.9
	55	180 ± 10	50 ± 10	2,420 ± 180	4	4.7	2.1
N150	13	1,960 ± 190	500 ± 50	22,450 ± 2,000	7.3	5.4	6.7
	31	900 ± 80	160 ± 15	13,370 ± 1,700	6.4	5.7	2.8
	55	250 ± 25	100 ± 10	1,025 ± 85	5.7	3.6	5.4
	83	130 ± 20	30 ± 10	1,130 ± 75	4.8	4.5	0.8

VOC	$p_L°$ (Pa)	α	β	References
Acetone	30,600	0.04	0.48	[22]
TCE	9,200	0.08	0.03	[9]
Toluene	3,800	0	0.14	[9]

*In order to calculate VdWi, EAi and EDi values, constants ($p_L°$, α, β) were used:

A possible explanation can be found in the adsorption behavior of toluene on the catalyst. Indeed, the prerequisite for catalytic VOC decomposition is that molecules must reach the catalyst interface, or at least contact a radical species formed within the boundary layer near the solid/gas interface [8]. On hydrophilic surface (such as most mineral oxides), the adsorption of water is hardly influenced by competing VOC. Water concentrations in indoor air are much higher than those of VOC; and due to strong hydrogen bonds between water and hydrophilic surfaces the affinity of water to hydrophilic surfaces is much stronger than that of organic molecules [21]. Therefore, the adsorption of organic molecules on hydrophilic surfaces is strongly determined by the presence of sorbed water. However, as far as we know, no fundamental data are available for VOC adsorption on the selected catalysts. Therefore, a detailed study on this partitioning process providing quantitative data is required to better understand the effect of RH on the toluene PPC removal.

3.3. Equilibrium sorption: effect of relative humidity

Equilibrium adsorption constants (K) of three relevant indoor air pollutants (toluene, acetone, trichloroethylene) have been determined using the EPICS methodology for three catalysts (Pd/Al_2O_3(b), N150, CuMn/TiO_2(b)) under different humidity levels. Results are represented in Table 1.

For all VOC-catalyst combinations, a logarithmic relationship can be observed between the partitioning constant and the relative humidity as exemplified by R^2 values higher than 0.950 (number of repetitions >4) (Fig. 5). However, K-values determined at dry air conditions did not fit to this logarithmic correlation, indicating that two different sorption mechanisms exist depending on the humidity level.

First, at humidity levels that do not result into a monolayer coverage of water molecules on the catalyst surface, a strong decrease of the equilibrium sorption coefficient with increasing RH is noticed. For example, the equilibrium partitioning coefficient of toluene on Pd/Al_2O_3(b) in dry air (62,500 ± 6000 mL g^{-1}) is reduced with a factor 12 at a relative humidity of 8%. Thus, the strong decrease of K at increasing RH may be explained by a competitive adsorption between water molecules and target VOC compounds for unoccupied catalyst sites since no water monolayer is formed yet [9]. Secondly, sorption equilibrium data obtained at ≥17% RH reveal that an other behavior can be observed for $PdAl_2O_3$(b) PPC. Indeed, for 17% RH the toluene partitioning coefficient on Pd/Al_2O_3(b) was determined as 1500 ± 200 L g^{-1} and 800 ± 50 for 31% RH which is only a reduction of a factor of 2. This is supported by Goodman et al. [23] who found that a complete monolayer of water is only adsorbed on an α-Al_2O_3 catalyst surface from 17% RH and 296 K. At humidity levels covering the catalyst surface with more than one monolayer of water, VOC can sorb on the water surface and/or dissolve in the bulk of this water film. Goss and Schwarzenbach [24] reported that mainly adsorption onto the surface of the adsorbed water film is dominating for the highest relative humidities.

Fig. 5 shows that, for toluene, the equilibrium sorption constants (K) and corresponding removal efficiencies (y) are logarithmically correlated for a constant energy density (e.g. $y = 15.4K - 42.1$ ($R^2 = 0.982$, $n = 4$)). This means that the highest VOC removal efficiencies in hybrid plasma catalyst configurations are expected for catalysts that favour VOC adsorption. This is an important conclusion for the synthesis, selection and production of catalysts suitable for PPC.

In order to better understand the sorption behavior of VOC on the (humid) catalyst surface, two kinds of interactions must be considered: (a) Van der Waals interactions (VdW) and (b) specific proton donor–acceptor (HD + HA) interactions [24]. The

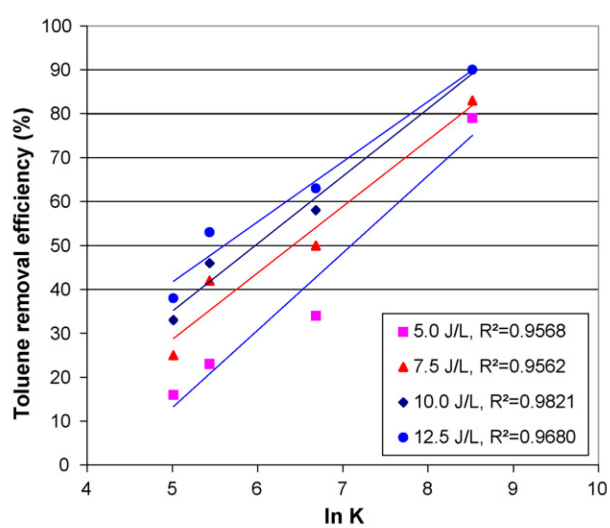

Fig. 5. Toluene removal efficiency (%) obtained with the Pd/Al_2O_3(b) catalyst at different energy densities (5.0, 7.5, 10.0, 12.5 J L^{-1}) (P = 101.3 kPa, T = 25 °C) as a function of the equilibrium sorption coefficient.

ability of a surface to interact with an adsorbate is dominated by the properties of its outermost molecular layer due to the exponential decrease of intermolecular interactions with distance and is quantified by the Van der Waals forces. Electron-donor/acceptor properties are connected to a change in the orientation of the adsorbed water molecules [24]. The VOC equilibrium partitioning coefficient between an air matrix and a mineral oxide surface, K, is related to the total free energy of adsorption ΔG_{ads} ($J\,mol^{-1}$) as [9]:

$$\Delta G_{ads}(J\,mol^{-1}) = -RT\ln[2.99\times10^{8}(m^{-1})K'] \qquad (6)$$

With K' ($m^3\,m^{-2}$) calculated from K ($mL\,g^{-1}$) and specific BET surface area ($m^2\,g^{-1}$) of the catalyst material. Based on thermodynamic parameters [9,25] a model was developed showing the total free energy of adsorption ΔG_{ads} ($J\,mol^{-1}$) as:

$$\Delta G_{ads}(J\,mol^{-1}) = (-5092 + 324.1\ln p_L^{\circ})\sqrt{VdW_{surf}} - 5071\beta\sqrt{HD_{surf}} - 3344\alpha\sqrt{HA_{surf}} \qquad (7)$$

where VdW_{surf}, HD_{surf}, HA_{surf} $(mJ\,m^{-2})^{0.5}$ characterize the ability of the surface to engage in Van der Waals, H-donor and H-acceptor interactions, respectively. Next, $p_L{}^{\circ}$, α and β are parameters that have been quantified for a large number of organic molecules by Howard and Meylan [26] and Abraham et al. [27] (Table 1).

From the equilibrium partitioning coefficient and $p_L{}^{\circ}$, α and β values given in Table 1, the surface parameters, VdW_{surf}, EA_{surf}, ED_{surf} could be calculated according to Eqs. (6) and (7). Since three unknown variables have to be calculated for each catalyst, a data set was obtained for three VOC being toluene, trichloroethylene and acetone (Table 1).

Obtained data reveal that the total free energy of adsorption ΔG_{ads} ($J\,mol^{-1}$) on Pd/Al_2O_3(b) and N150 catalysts of more apolar compounds such as toluene and TCE, is mostly due to Van der Waals interactions (77 and 84%, respectively). While for acetone sorption (more polar compound) both van der Waals (39%) and H-donor interactions (58%) are important.

It can be concluded that the negative humidity effect during PPC is largely determined by VdW interactions. Indeed, Table 1 reveals that the decreasing K values can be correlated with VdW values. Highest K values, and thus highest VOC removal efficiencies for Pd/Al_2O_3(b) PPC, are obtained in dry air (RH < 1%) where a VdW_{surf} value of 10.2 $(mJ\,m^{-2})^{0.5}$ was calculated. This value is confirmed by measurements of Goss and Schwarzenbach [24] who reported that the VdW values of a dry mineral surface are in the range of 8–10 $(mJ\,m^{-2})^{0.5}$. Table 1 also shows VdW_{surf} values for Pd/Al_2O_3(b) decreasing by a factor of 2.5 for RH ranging up to 55%. Generally, it is accepted that at 100% RH VdW_{surf} values are equal to those of bulk water surface VdW forces being around 4.67 $(mJ\,m^{-2})^{0.5}$. Since VdW_{surf} value at 55% RH are in this range (Table 1), it can be concluded that the Pd/Al_2O_3(b) catalyst is covered with multilayers of water, consequently minimalizing direct catalyst/VOC intermolecular interactions. Similar trends were seen for the N150 catalyst (VdW_{surf} = 4.8 $(mJ\,m^{-2})^{0.5}$).

Although H-donor interactions also prove to have an important contribution to the total free energy of adsorption (especially for more polar compounds), no correlation can be made between HD_{surf} and the decreasing K values as a function of humidity. Therefore, it can be postulated that even for more polar compounds (e.g. acetone) similar effects of humidity on the PPC efficiency will be observed. However, since the humidity-independent H-donor interactions are more important than VdW interactions for these compounds, this negative effect is expected to be less pronounced.

4. Conclusion

In this paper ozone and toluene removal is investigated using six different catalysts in post-plasma configuration. It is proven that the ozone removal efficiency is strongly correlated with the active compound of the tested catalysts. For the tested catalysts, the effect of humidity on ozone abatement was negligible.

This study revealed differences in toluene removal efficiency for the different catalysts even when identical masses of ozone were converted. This is for example the case for $CuOMnO_2/TiO_2$(a) and N140, having a toluene removal efficiency of 25 and 4% at an energy density of 4 $J\,L^{-1}$, respectively. This reveals that not the amount of converted ozone, but VOC sorption is one of the most critical parameters determining the efficiency of catalytic VOC oxidation.

Equilibrium adsorption constants K of different catalyst were determined using EPICS methodology. Significant differences were measured between several catalysts. Next it was proven that the K values strongly decreased with increasing humidities. For Pd/Al_2O_3(b) the equilibrium adsorption constant was 12 times lower at 8% RH in comparison with that in dry air ($62{,}500 \pm 6000\ mL\,g^{-1}$). A logarithmic correlation is found between equilibrium sorption constants and corresponding toluene removal efficiencies, explaining the observed differences at dry or humid condition between the tested catalysts.

Finally, it is concluded that the humidity effect on sorption and thus PPC is largely determined by VdW interactions.

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